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(54) Glass compositions

(57) A fluoride glass for use in the production of optical fibres has an enhanced D/H ratio, preferably such that OD:OH is at least 9:1.

In the Example, such a glass is prepared by treating with D₂O a melt comprising 51.53 mole per cent ZrF₄, 20.47 mole per cent BAF₂, 5.27 mole per cent LaF₃, 3.24 mole per cent AlF₃, and 19.49 mole per cent LiF.

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SPECIFICATION

Glass compositions

5 This invention relates to glass compositions. In particular, it relates to compositions which are suitable for use in the production of optical fibres. Multi-component oxide glasses are presently used in the preparation of optical fibres. Examples of glasses
10 of such compositions are the borosilicate, aluminosilicate and germanosilicate glasses. Their compositions comprise, respectively, B_2O_3 , Al_2O_3 and GeO_2 , as well as SiO_2 and an alkali metal oxide such as Na_2O as the three primary components. Such compositions can be drawn, e.g. by the double-crucible technique, into fibres comprising a core and a cladding, the refractive indices of core and cladding being chosen such that light at a certain wavelength can be transmitted along the core.

20 The distance over which a signal can be successfully transmitted through an optical fibre is limited by two distinct types of loss which occur in glasses generally: losses arising from absorption, e.g. in electronic transitions or vibrational transitions; and
25 losses due to Rayleigh scattering (a phenomenon resulting from inhomogeneities). The latter type of loss is a theoretically inevitable one, although it becomes far less significant at longer wavelengths. If a glass can be formulated so that the absorption is very low at long wavelengths, very low loss (absorption plus Rayleigh scattering) can be achieved in communications at such wavelengths. In borosilicate glasses, the absorption spectrum is such that they have minimum loss in the range of 0.8-1.2 μm .
30 Such glasses are less suitable for long than for short distance communication, e.g. between computers.

A loss minimum at about 800 nm is clearly shown for sodium germanosilicate and sodium borosilicate glasses in, for example, Figure 1 of Spierings, J. Mat. Sci., 14 (1979) 2919-2923. Primary absorption peaks are observed at about 950 nm, and their presence is attributed to OH vibrational absorption. Spierings discloses that, if a gas containing D_2O is bubbled through the melt of an alkali metal germanosilicate
45 glass, there appears to be an exchange of D for H atoms. There is a consequent decrease in absorption at about 960 nm and a corresponding increase in absorption at about 1300 nm attributable to OD absorption. Consequence of this ion-exchange is
50 that the tails of the reduced OH absorption band contribute less to loss in the fibre in the 800 to 900 nm range.

Other procedures are known for reducing the OH concentration in oxide glasses. These also involve
55 the passage of gases through the glass melt, such gases being CO/CO_2 (GB-A-1507712), dry oxygen (GB-A-2033373) and chlorides such as $SiCl_4$ (JP-A-56-149332). European Patent Application No. 83305066.9 describes fluorine-containing gases, e.g.
60 C_3F_8 and F_2 , as drying agents.

By these various means, it has been sought, in theory or practice, to reduce the absorption losses inherent in optical fibres. The alternative procedure has been, as suggested above, to reduce Rayleigh
65 scattering by formulating glasses which can be

operated at longer wavelengths. Silica glasses have loss minima at 1.3 and 1.55 μm and are already being manufactured and used for long distance communication. More recently, fluoride glasses
70 have been prepared which, it is suggested, might be operated in the 2 to 10 μm range. It seems more likely that, in the immediate future, the operational range for such fibres will be of the order of 3 μm . As operational wavelengths increase, there is corresponding difficulty in formulating suitable lasers.

Multi-component fluoride glass compositions which have been formulated include BeF_2 and $ZnCl_2$ but, more recently, ZrF_4 -based glasses have been discovered and their use is preferable. Examples of components of such compositions are, in addition to ZrF_4 (or HfF_4), BaF_2 , LaF_3 , GdF_3 , AlF_3 and LiF . Particular compositions, and a general background to the formulation of non-silica-based infra-red fibres, are given by Miyashita *et al.*, IEEE Journal of
80 Quantum Electronics, QE-18, No. 10 (October 1982).

Some multi-component halide glasses are exemplified in Table 1 of the article by Miyashita *et al.* Suitable compositions can be determined from phase diagrams of the type given for a ZrF_4 - BaF_2 -
90 GdF_3 composition in Figure 3 of the article by Miyashita *et al.*

Figure 20 of the article by Miyashita *et al.* shows the absorption loss for a particular optical fibre whose core and cladding are fluoride glasses. The
95 absorption minimum is 2.55 μm , with an absorption peak at 2.9 μm . This broad peak can contribute to loss in operation at the absorption minimum. Its existence can be ascribed to the fundamental OH stretch vibration frequency. OH and also HF bonds are inevitably present in fluoride glasses prepared by conventional procedures, although the concentration of the former particularly may be reduced by chemical vapour deposition. HF lasers operate at 2.8
100 μm .

A fluoride glass composition according to the invention contains an enhanced D/H ratio. In other words, a composition of the invention, e.g. any multi-component fluoride glass composition of the type described above, has a higher deuterium
110 concentration than would have been the case if prepared from components where no steps had been taken to replace any hydrogen atoms by deuterium atoms. Preferably, in a composition of the invention, there are more OD than OH bonds. More preferably, the OD:OH ratio is at least 3:1 and most preferably at least 9:1. Ideally all, and in practice substantially all, hydrogen atoms in OH bonds can be in the 2H , i.e. deuterium, form.

It is also preferred that hydrogen atoms in a
120 composition, present other than as hydroxyl, should be in the deuterium form, at least in an enhanced ratio and more preferably in the higher ratios described above for the D/H ratio in hydroxyl groups. Thus, for example, it is preferred that hydrogen
125 present in the composition as a result of the presence in its raw components, or introduced by the passage of, say, drying or reducing gases, should be in the D form. For example, it is preferred that HF, H_2 , CHF_3 or $CHCl_3$ should rather be present,
130 or used, in a deuterated form.

The degree of enhancement in accordance with the invention can be reckoned from the relative absorptivity of compositions in which there has, or has not been enhancement. For example, the degree of OH replacement by OD can be reckoned from the decrease in OH absorption at about 2.7-2.8 μm and the corresponding increase in OD absorption at about 3.8 μm . This particular change reduces the loss of an optical fibre operated at an absorption minimum close to the characteristic OH absorption. It is thought that absorptions other than that of OH may also contribute to losses in optical fibres prepared from fluoride compositions operated at their absorption minima, at least in the present operating range of about 2.5-3.5, and especially 2.6-3.0, μm . This reduction in absorption loss, combined with the inevitable reduction in Rayleigh scattering by comparison with the use of fibres made from silica-containing compositions, as the result of operation at longer wavelengths, allows the production of optical fibres of particular suitability for use in long distance communication, without the need for multi-stage amplification.

A composition of the invention may be prepared by modification of a known fluoride glass composition or such as composition prepared from components which do not have an enhanced D/H ratio. The use of components having an enhanced D/H ratio may be possible, although H_2O or other H-containing materials are impurities in any case.

OH may be replaced by OD by simple ion-exchange. For example, D_2O may be passed over a fluoride glass melt. It is conventional to contact an inert gas with a glass melt, and D_2O may simply be included with the inert gas, with the consequent desired exchange in the composition. Continual passage of D_2O can raise the OD/OH ratio above its equilibrium value.

The inert gas may be argon or nitrogen. The conditions of passage may be conventional.

H may also be replaced by other exchange reactions. HF may be used as a drying agent, and also to remove oxide impurities, but may be incorporated in the glass composition. HF absorbs in the 2-3.5 μm region. DF may be used instead, e.g. alone or subsequent to the use of D_2O . The use of DF may generate OD which can ion-exchange with OH. The result is that losses can be minimised in the 2-3.5 μm region, DF and OD absorption peaks being at about 3.8 and 3.9 μm .

Other drying agents of potential use include CHCl_3 and CHF_3 . In accordance with the invention, it is preferred that they are replaced by CDCl_3 and CDF_3 .

Components for fluoride glasses are often prepared using ammonium bifluoride. In accordance with the invention, a deuterated reactant is preferably used, e.g. NH_4DF_2 or ND_4DF_2 .

It will often be desirable to combine ion-exchange of OH groups to OD groups by the method described above with a subsequent means of reducing the OD concentration. Thus, an inert gas such as nitrogen or argon combined with D_2O may achieve the primary object of the invention but gives a composition containing excess D_2O . The excess may then be removed by replacement of the D_2O in the drying

schedule by, say, DF.

It is often desirable to adjust the redox potential of a glass composition. The potential can be determined to an extent by the nature of the glass components. Alternatively or in addition, a reducing gas may be passed over a glass melt; while H_2 has been avoided, CO (as described above) is one example of a suitable gas for use with an oxide glass. According to the present invention, D_2 may be used.

In general, therefore, a fluoride glass composition can be modified by a process which comprises bringing a melt of the composition into contact with a deuterium-containing compound. This may be achieved in a conventional schedule of the type used for bubbling gases through borosilicate glasses (see EPA 83305066.9, for example), although bubbling is not necessary in this case. It appears that passage or contact of a suitable deuterium compound over or with a fluoride glass melt, can achieve the desired degree of D \rightarrow H exchange or reaction.

Compositions of the invention can be formulated into bulk glasses or preforms for subsequent drawing into optical fibres. Fast quenching may be necessary. Chemical vapour deposition may be used.

The production of fluoride glass fibres can be by the methods described by Miyashita *et al.*, *supra*. These methods can be used or suitably modified for the production of fibres having a core and a cladding, e.g. from a double-crucible or by casting; see also Mitachi *et al.*, *Electron Lett.* 18 (Feb. 1982) 170-171. Both core and cladding may be of compositions of the invention. Their respective dimensions may be a diameter of 50 to 220 μm , and an outer diameter of at least 25 μm more, e.g. 100 to 270 μm . Optical fibres of the invention may have low loss, e.g. less than 20 dB/km (at 2.8 μm).

The following Example illustrates the invention.

Example

A glass composition (40 g) was prepared from ZrF_4 , BaF_2 , LaF_3 , AlF_3 and LiF. The respective molar (and weight) percentages were 51.53 (61.40), 20.47 (25.56), 5.27 (7.47), 3.24 (1.94) and 19.49 (3.60). It was melted by heating to 850 C under nitrogen (flow rate 3 l/min). After 2.5 hours at this temperature, D_2O was also passed for 1 hour. The composition was annealed at 240 C and air-quenched for 10 min after cooling to 240 C.

Water absorption was observed from infra-red spectroscopy of the bulk glass. This measurement may be influenced by water not present in the glass. The loss was less than 500 dB/km at 2.8 μm . An OD peak (850 dB/km) was observed at 3.87 μm .

For the purposes of comparison, 40 g of the same glass composition were heated to 850 C under argon (3 l/min) and removed after a further 2.75 hours (900 C recorded after 1.25 hours). The composition was annealed at 240 C and quenched for 12 min. A loss of 1500 dB/km was observed at 2.8 μm .

CLAIMS

1. A fluoride glass composition which contains

an enhanced D/H ratio.

2. A composition according to claim 1, in which the OD:OH ratio is at least 9:1.

3. A process for treating a fluoride glass composition, which comprises bringing a deuterium-containing compound into contact with a melt of the composition.

4. A process according to claim 3, in which the compound is selected from D_2O , D_2 , DF , $CDCl_3$ and CDF_3 .

5. A process according to claim 3, which comprises contacting the melt with, sequentially, D_2O and DF .

6. A fluoride glass composition obtained by a process according to any of claims 3 to 5.

7. An optical fibre of a composition according to any of claims 1, 2 and 6.

8. An optical fibre according to claim 7, comprising a core and a cladding, the core having a loss of less than 20 dB/km.